

# Giant diamagnetism in half-metallic Co<sub>2</sub>CrAl Heusler alloy

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A giant diamagnetism in the Co<sub>2</sub>CrAl compounds, in both bulk and thin film, below a certain temperature ( $T_z$ ) was observed. Above  $T_z$ , the compound behaves as an ordinary ferromagnet. The diamagnetic alignment might be initiated by the Landau diamagnetism because of the half-metallic properties and the pinning of the diamagnetism is preserved by the peculiar electronic structures.

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Diamagnetism (DM) is a material property originating from the response of an ensemble of charged particles governed by the Faraday-Lenz law. Although it is ubiquitous to all materials, it is usually masked by much stronger paramagnetism (PM) or ferromagnetism (FM). Although some materials exhibit DM, the strength is very weak. The only exceptions are superconductors in which the magnetic field is completely expelled below the superconducting transition temperature. This effect is known as the Meissner effect.

According to the celebrated Bohr-van Leeuwen theorem [1], the orbital DM is impossible in classical thermodynamics, since the 'skipping-orbit' of electrons near the surface cancels exactly the bulk contribution to the diamagnetic moment. Later, by applying quantum mechanics, Landau [2] showed that the bulk and the surface contributions were not balanced, for DM to survive. Even for free-electron gas, however, the Landau DM is only 1/3 of the Pauli PM. Consequently, the Landau DM cannot be observed.

Although the Landau DM is too weak to be observed, a giant DM, *i.e.*, a magnetic susceptibility comparable to -1, is not very rare. Claus and Veal [3] observed a large negative susceptibility in a weakly ferromagnetic Pd-0.5at.% Fe alloy upon field cooling (FC) under a very low field (a few tens of mG) and concluded that the negative susceptibility was due to the inhomogeneity of sample. This anomaly disappeared after removal of the surface layer by grinding and chemical etching. The greatly negative susceptibility was also noticed in a Pr-Al-Ni-Cu-Fe metallic glass during the zero-field-cooled (ZFC) magnetization measurement [4]. It was due to the residual magnetic field of magnet in the SQUID magnetometer, which was not supposed to exist. A negative magnetic susceptibility observed in the FC branch of spin- and charge-doped (Sr,La)(Ti,Co)O<sub>3</sub> was explained by the existence of two magnetic sublattices and the superposition of FM and PM to the magnetization [5]. These are not relevant to the Landau DM, but to some artifacts originating from the measurements and the material prepa-

ration.

We found the peculiar magnetic properties of Co<sub>2</sub>CrAl Heusler alloy, both in bulk and thin films. The FC magnetization is typical for the ferromagnetic material, while the ZFC magnetization exhibits a giant negative magnetization, a hallmark of extraordinary DM, at low temperatures and the magnetization direction is flipped abruptly at a certain temperature upon heating. The magnitude of negative magnetization is comparable to that of the FC magnetization at the same temperature. The flipping temperature strongly depends on the field strength. We attribute this giant DM to the interplay between Landau DM and peculiar electronic structures which are closely related to the half-metallicity of Co<sub>2</sub>CrAl Heusler alloy.

Bulk Co<sub>2</sub>CrAl alloy was prepared by melting high purity elements (99.99%) in an arc furnace with a water-cooled Cu hearth. The ingot was remelted 5 times and annealed at 1273 K for 10 h in vacuum to promote the volume homogeneity. No weight loss after melting and heat treatment was observed. The alloy composition was confirmed by x-ray fluorescence. Co<sub>2</sub>CrAl alloy films were prepared by flash evaporation of the crushed alloy powders of 80 - 100  $\mu$ m in diameter onto glass substrates in a vacuum better than  $2 \times 10^{-5}$  Pa. The alloy powders were prepared from the same ingot of bulk Co<sub>2</sub>CrAl alloy. To enhance the crystallinity of film, the substrate was kept at 708 K during deposition (film 1). Another film was deposited at 150 K and post annealed at 760 K for 10 min (film 2). The thicknesses of films are 135 and 153 nm for film 1 and 2, respectively. The magnetic properties were investigated in a temperature range of  $5 \leq T \leq 350$  K using a SQUID magnetometer for the samples cooled in FC and ZFC modes, respectively.

Figure 1 presents the temperature dependence of magnetization,  $M(T)$ , of the bulk sample. The Curie temperature  $T_C$  was 334 K. The  $M(T)$  behavior of the bulk sample measured at 100 Oe in the FC branch displays that of a typical ferromagnet and the ZFC one is also typical for a ferromagnet with some local structural dis-

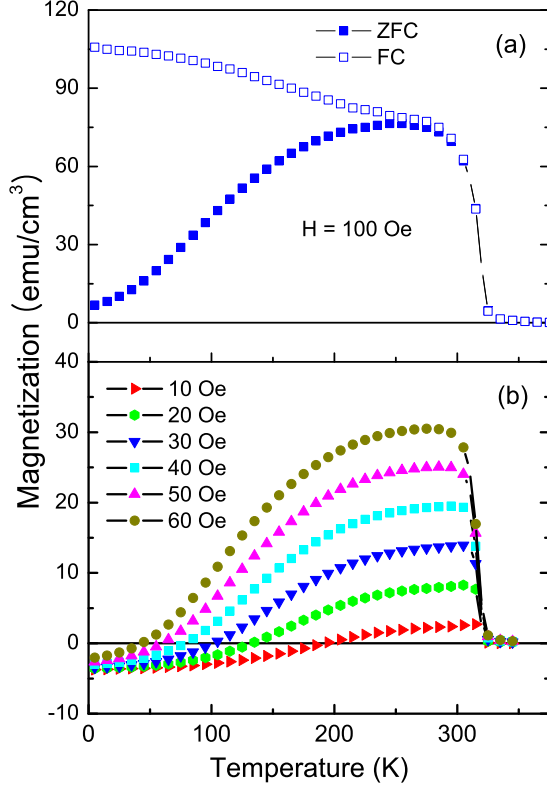


FIG. 1: (Color online) Temperature dependence of the magnetization of the bulk Co<sub>2</sub>CrAl alloy. (a) FC and ZFC curves at  $H = 100$  Oe and (b) ZFC curves at various applied fields.

order [Fig. 1(a)]. However, as the external magnetic field decreases below 100 Oe, the ZFC curves show significantly diamagnetic behavior at low temperatures. The magnetization changes its sign at a certain temperature designated as  $T_z$ . As the strength of measuring field increases,  $T_z$  decreases. Since the investigated sample did not exhibit any superconducting behavior down to 5 K, we can safely exclude the superconductivity as the origin for the observed DM.

The diamagnetic behavior in the ZFC mode at low temperatures is more prominent for the thin films. In Fig. 2 the ZFC magnetization curves for film 1 at various magnetic fields are displayed. In the thin-film samples, the strength of DM is nearly comparable to that of the FC magnetization at the same temperature.

In Ref. 3, a large negative susceptibility observed in the FC branch at very low fields was due to the inhomogeneity of sample. In our case the large DM was found in the ZFC branch and the applied field for measurement was much larger than that of Ref. 3. Therefore, the inhomogeneity of sample is excluded as the reason for the observed diamagnetic behavior.

Since a non-zero but negative residual field of the su-

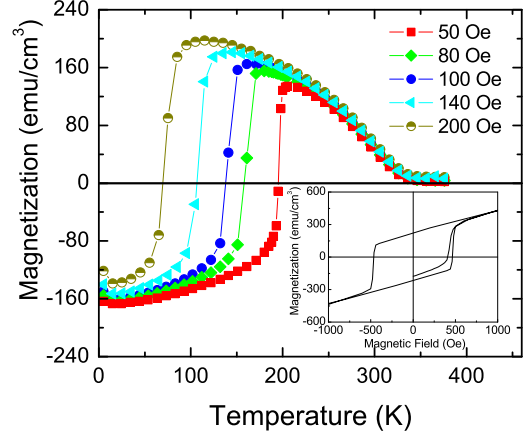


FIG. 2: (Color online) Dependence of ZFC  $M(T)$  for film 1 at various applied magnetic fields. The inset shows the initial rising curve of film 1.

perconducting magnet during cooling is another possible reason for the observed DM [4], we have checked the residual field. It was +1.5 Oe, which is positive. Furthermore, if the direction of applied field is flipped during the measurement after ZFC, a large positive magnetization was observed and became negative above  $T_z$ . Therefore, the observed giant DM is not due to the residual field of SQUID magnetometer during cooling.

As aforementioned, every material can exhibit a diamagnetic behavior. Once the magnetic field lines start to penetrate a metallic sample, there are induced currents on the sample surface. According to the Faraday-Lenz law, the induced current generates a magnetic field opposing the applied field. If the induced currents persist, they would expel the magnetic field completely out of the interior of sample. In the normal metal, however, the finite resistance kills the current instantly and, consequently, the magnetic field can penetrate into the interior of sample. Therefore, the DM is hardly observed in most of metallic materials.

If a magnetic field is applied to a metal, the majority (minority) bands move downward (upward) since the energy  $-\mu \cdot \mathbf{H}$  is added to the system, where  $\mu$  is the magnetic moment of an electron and  $\mathbf{H}$  the applied magnetic field. Accordingly, the Fermi level, more precisely, the chemical potential for the majority (minority) band moves downward (upward). Then, to equilibrate the chemical potential, the electrons in the minority bands near the Fermi level flip their spins and fill up the majority bands until the Fermi level becomes uniform. This is the well-known Pauli PM, which is three times stronger than the Landau DM even in free-electron gas. In the ordinary ferromagnet, when a magnetic field is applied to measure the magnetization, the Pauli paramagnetic response would lead

to the alignment of magnetic moments inside the sample along the applied field.

On the other hand, in half metals, such as  $\text{Co}_2\text{CrAl}$ , the Pauli PM cannot occur since there is no Fermi-level imbalance under an applied field because of the absence of minority bands near the Fermi level in  $\text{Co}_2\text{CrAl}$ . Therefore, the Landau DM might be disclosed. This initial DM somehow pins the magnetic moments in the interior of sample opposing the applied field, resulting in a huge negative magnetization, as observed in our sample. The apparent DM is destroyed by the applied field with a strength higher than a certain value since the sample is supposed to be a ferromagnet and, hence, the higher the applied field, the stronger the tendency for the alignment of magnetic moments along the applied field. Once the whole magnetic moments in the sample are completely aligned, the Landau DM would be masked by the ferromagnetic response and, consequently, the sample behaves as an ordinary ferromagnet. This is clearly seen in the initial rising curves of hysteresis of the bulk and the film samples (see the inset of Fig. 2). The initial rising curves start with a negative magnetization and become positive above a certain critical magnetic field. After the positive magnetization is achieved, the sample comes to be an ordinary ferromagnet.

The decrease of  $T_z$  with increasing applied field can be understood as follows. The magnetic moments of individual domains are well aligned opposite to the applied field and are ‘frozen’ at low temperatures. Therefore, it is hard to flip the magnetization to align along the applied field. The energy required to flip the magnetization of a single domain is  $\Delta E = K_A V$ , where  $K_A$  is the magnetic anisotropy constant and  $V$  is the volume of domain. This energy can be supplied thermally. As temperature increases, the magnetic moments tend to align along the applied field more easily since the magnetic moments are more agitated owing to the supplied extra thermal energy. This leads to the decrease in the magnitude of negative magnetization. If temperature reaches a certain temperature, the magnetic moments flip their directions as a whole. When an external field is applied, the energy barrier for magnetization flipping is reduced to be  $\Delta E = K_A V \left(1 - \frac{M_s H_c}{2K_A}\right)$ , where  $M_s$  is the saturation magnetization and  $H_c$  is the coercive field. According to the Néel-Brown model of magnetization reversal [6]

$$\frac{H_c(T)}{H_c(0)} \cong \left[1 - \left(\frac{T}{T_0}\right)^\alpha\right], \quad (1)$$

where  $H_c(0) \equiv \frac{M_s}{2K_A}$  is the coercive field at 0 K,  $T_0 = \frac{K_A V}{k_B}$  ( $k_B$  is the Boltzmann constant), and  $\alpha$  a constant which depends on the average angle between magnetic moments and applied field [7]. At  $T = T_0$ , the coercive field is zero.

$T_z$  is the temperature at which the magnetization reversal takes place under a given magnetic field. There-

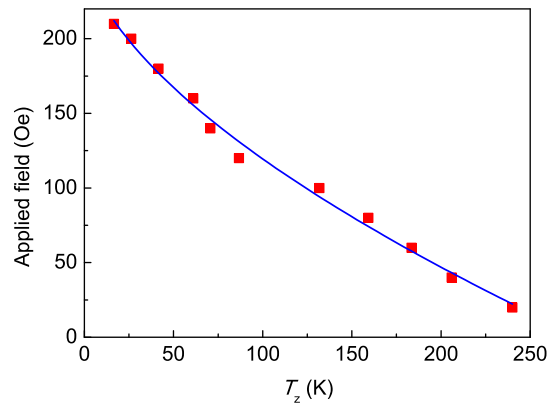


FIG. 3: (Color online) Applied field as a function of  $T_z$  for the bulk sample. Solid lines are the fitting result.

fore, we can treat the applied field as the coercive field at  $T = T_z$ .  $\alpha$  is a fitting parameter:  $\alpha = 0.602$  for the bulk sample and 0.522 for film 2, while 0.254 for film 1. Although  $\alpha$  is usually close to  $2/3$ , it can be as small as 0.5, depending on the average angle between magnetic moments and the applied field. Therefore, the magnitudes of  $\alpha$  for the bulk and film 2 are reasonable in a sense that the Néel-Brown model is applied, however, it is too small for film 1. The x-ray diffraction investigation (see Fig. 2 in Ref. 9) reveals that film 1 has a significantly worse crystallinity than film 2. Film 1 has a smaller grain size, and a great amount of intergranular amorphous phase which plays an important role in determining the coercive field [10], resulting in a different temperature dependence of the coercivity from that of the bulk and film 2.

Even if we accept the scenario explained here, one might ask another question, such as “*What kind of ‘force’ can initially hold or pin the magnetization opposite to the applied field?*” We argue that the pinning of diamagnetic magnetization is due to the peculiar electronic structures. We calculated the electronic structures of  $\text{Co}_2\text{CrAl}$  compound under various conditions by using the *WIEN2k* package [11]. For the exchange-correlation functional, the generalized-gradient-approximation version of Perdew *et al.* [12] was used. The *WIEN2k* package has a special feature that the magnetic field can be added in the course of self-consistent iterations and the direction of applied field can be virtually arbitrary. Since the spin-orbit coupling is crucial for this calculation, it is included. Since the magnitude of energy difference we deal with is very tiny, the whole reciprocal unit cell was divided into  $50 \times 50 \times 50$  parallelepipeds to safely handle the subtle energy difference. We also vary the direction of applied field.

Once the magnetization direction is chosen, say, in the (001) direction, the field is applied in the same (opposite) direction. Hereafter, we will refer it to the FM (DM) magnetization. In the ordinary ferromagnetic ma-

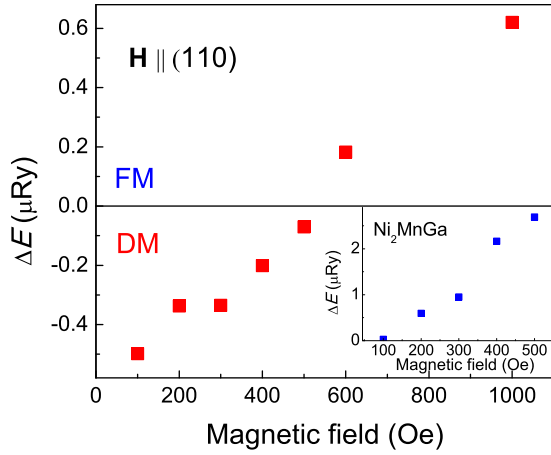


FIG. 4: (Color online) Total energy difference between ferromagnetic and diamagnetic states. Inset shows the same except for  $\text{Ni}_2\text{MnGa}$ .

terial, when an external magnetic field is applied, the total energy is lower than the case without the applied field by aligning the magnetic moments along the field. If the magnetic field is applied opposite to the magnetization direction, the opposite phenomenon happens and the total energy becomes higher. As seen in the inset of Fig. 4, the total energy difference of  $\text{Ni}_2\text{MnGa}$  compound is always positive and increases according to the field strength. The total energy difference  $\Delta E$  is defined as  $\Delta E \equiv E_{\text{tot.DM}} - E_{\text{tot.FM}}$ . Positive implies that the ferromagnetic state is more stable than the diamagnetic one. Therefore, in the ordinary ferromagnet, the diamagnetic alignment is impossible.

The situation becomes quite different if the same calculation is done for the  $\text{Co}_2\text{CrAl}$  compound. In Fig. 4, the total energy of the DM is lower than the FM when the applied field strength is smaller than 500 Oe. Our calculational results also reveal that the diamagnetic state is the ground state when an applied field is lower than 500 Oe at 0 K. This peculiar electronic structures of  $\text{Co}_2\text{CrAl}$  compound are the source of pinning the DM unless a sufficient thermal energy is supplied to agitate the magnetic moments to finally align along the applied field. Even though the diamagnetic response might be small, it is

strong enough to pin the magnetic moments within the thin-film sample, similar to the case exhibited in Ref. 3.

We observed a giant DM in the  $\text{Co}_2\text{CrAl}$  compound at low temperatures. The phenomenon is persistent up to a certain temperature  $T_z$  which increases as the magnetic field strength decreases. The diamagnetic alignment at low  $T$  might be initiated by the Landau DM, owing to the absence of minority bands at the Fermi level, and the pinning of the DM is preserved by the peculiar electronic structures of the compound. Although the celebrated Landau DM is predicted more than 70 years ago, it had not been possible to be observed since it is masked by stronger PM or even FM. The interplay between half-metallicity and peculiar electronic structures of the  $\text{Co}_2\text{CrAl}$  compound enables us to observe this old puzzle of magnetism.

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- [1] N. Bohr, Dissertation, Copenhagen (1911); J. N. Van Leeuwen, J. Phys. Radium **2**, 361-377 (1921).
- [2] L. D. Landau, Z. Phys. **64**, 629 (1930).
- [3] H. Claus and B. W. Veal, Phys. Rev. B **56**, 872 (1997).
- [4] Y. T. Wang *et al.*, Appl. Phys. Lett. **85**, 2881 (2004).
- [5] J. Yang *et al.*, Appl. Phys. Lett. **91**, 052502 (2007).
- [6] W. Wernsdorfer *et al.*, Phys. Rev. Lett. **78**, 1791 (1997).
- [7] M. P. Sharrock, IEEE Trans. Magn. **44**, 4414 (1999).
- [8] H. Pfeiffer, Phys. Stat. Sol. **118**, 295 (1990).
- [9] Y. V. Kudryavtsev *et al.*, Phys. Rev. B **77**, 195104 (2008); K. W. Kim *et al.*, J. Korean Phys. Soc. **53**, 2475 (2008).
- [10] K. Suzuki and J.M. Cadogan, Phil. Mag. Lett. **77**, 371 (1998).
- [11] P. Blaha *et al.*, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Techn. Universität Wien, Wien, Austria, 2001).
- [12] J. P. Perdew *et al.*, Phys. Rev. Lett. **77**, 3865 (1996).